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# Enhanced thermoelectric properties of the flexible tellurium nanowire film hybridized with single-walled carbon nanotube

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ABSTRACT

Thermoelectrics is a challenging issue for future energy harvesting and cooling technology. We here have demonstrated a new system of the tellurium nanowire (TeNW) films hybridized with single-walled carbon nanotube (SWCNT) as a flexible thermoelectric material and investigated their thermoelectric properties as a function of SWCNT weight ratio in the hybrid. The excellent mechanical stability and electrical conductivity of SWCNT enhance the flexibility and thermoelectric properties of the pure TeNW film. The addition of 2 wt% SWCNT into TeNW matrix significantly increases the electrical conductivity from 4 to 50 S $m^{-1}$ while maintaining the high thermopower, thereby leading to one order of magnitude higher figure of merit (ZT) compared to the pure TeNW film. These results indicate that the SWCNT/TeNW hybrid film would be promising for a potential use as a flexible thermoelectric material.


## 1. Introduction

Thermoelectric (TE) materials have been attracted because of their large potentials to both energy harvesting and electronic cooling devices [1–4]. The performance of TE material is evaluated by Figure of merit, given by

$$ZT = (S^2\sigma)T\kappa^{-1} \quad (1)$$

where $S$, $\sigma$, T, and $\kappa$ are the thermopower, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Thus, the high $S$ and $\sigma$ with low $\kappa$ are desirable for high ZT. However, the design to get high ZT is not easy because these three factors are interdependent and lie in a trade-off relation [5]. In general, inorganic semiconductors are promising TE materials due to their intrinsic high thermopower derived from their crystalline structure [6–9], so many studies on the inorganic semiconductors or their alloys with high ZT have been reported. However, they still have low electrical conductivity, and furthermore have some drawbacks which are the scarcity of raw materials, chemical/mechanical unstability, expensive cost and processing rigidity of brittle materials [6,10]. In this study, as one of the promising approaches to overcome these limitations, we suggest a flexible hybrid system including the 1-D inorganic semiconductor with high thermopower such as tellurium nanowire (TeNW) and single-walled carbon nanotube (SWCNT) with high electrical conductivity.

Several approaches for flexible TE materials have already been investigated in order to overcome the limitations of inorganic semiconductors. The early researches focused on the properties of homogeneous materials such as conducting polymers [11,12] or nanocarbons [13–16], and more recently the hybrid systems composed of more than two materials have been studied [17]. Some carbon nanotube (CNT)/polymer hybrid systems for flexible TE materials have been reported [18–20]. They have shown the light weight, flexibility and high electrical conductivity due to CNT, but their TE performance has been unsatisfactory due to the low thermopowers of CNT and polymers. Inorganic semiconductor/conducting polymer hybrid systems have also been suggested for improved TE performance [21–24]. TeNW/water-soluble PEDOT:PSS hybrid system has shown the enhanced thermopower and electrical conductivity, thereby leading to higher ZT compared to PEDOT:PSS or TeNW itself [23,24]. However, the mechanical/chemical stability of this hybrid film has not been satisfied for flexible TE devices [25].

Therefore, we have proposed a new method to fabricate a flexible SWCNT/TeNW hybrid film, in which SWCNT and TeNW have been selected due to their high electrical conductivity and thermopower, respectively. The effects of the weight ratio of SWCNT in hybrid system on the TE performance have been

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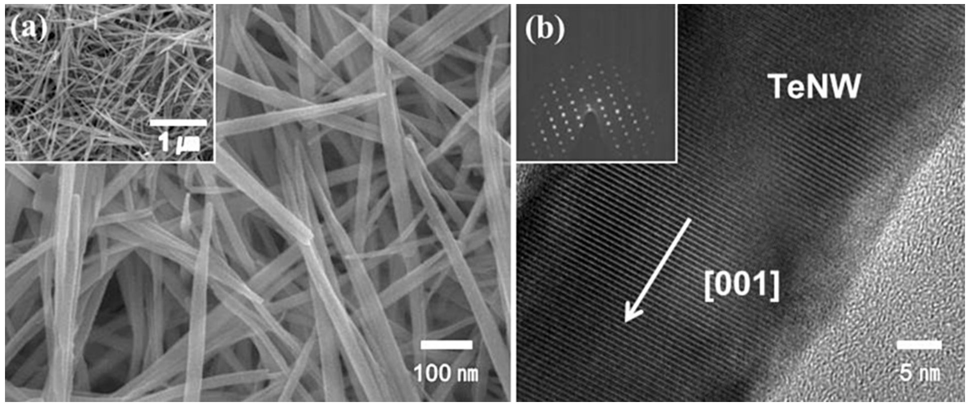


**Fig. 1.** (a) FE-SEM and (b) TEM images of the synthesized TeNW.

systematically studied. We have demonstrated that the 2 wt% addition of SWCNT into TeNW matrix results in the significant increase of the electrical conductivity maintaining the high thermopower and slight decrease of the thermal conductivity, thereby leading to one order of magnitude higher ZT compared to the pure TeNW film.

## 2. Experimental details

TeNW was synthesized by the typical procedure reported in the previous literature [26]. All chemicals were purchased from Sigma–Aldrich and used without further purification. 1.0 g of ascorbic acid ($C_6H_8O_6$) and 0.1 g of cetyltrimethylammonium bromide (CTAB, 0.2 mmol) were dissolved in distilled water (40 mL). And 0.052 g (0.25 mmol) of sodium tellurite ($Na_2TeO_3$) was added to the solution under vigorous stirring, forming a white suspension. The suspension was heated to 90 °C and reacted for 20 h, followed by several washings with DI water and ethanol to remove the excess CTAB. Synthesized TeNW was dried in oven for overnight. For hybrid film preparation, 10 mg of TeNW was re-dispersed in DI water with each volume of SWCNT (AST-100F grade, Hanwha nanotech.) solution. 1 wt% of sodium dodecyl sulfate was added to the solution with ultra-sonification for 10 min for well dispersion. Then, the hybrid film was fabricated under vacuum filtration of the mixed solution on 0.22 μm PVDF filter, washed intensively to remove the used surfactant and dried in a vacuum oven for overnight.

The morphology of the hybrid film was characterized by FE-SEM (JSM-6701F, JEOL) and HR-TEM (Tecnai F20, FEI). The distribution of SWCNT in the TeNW matrix was characterized using Raman

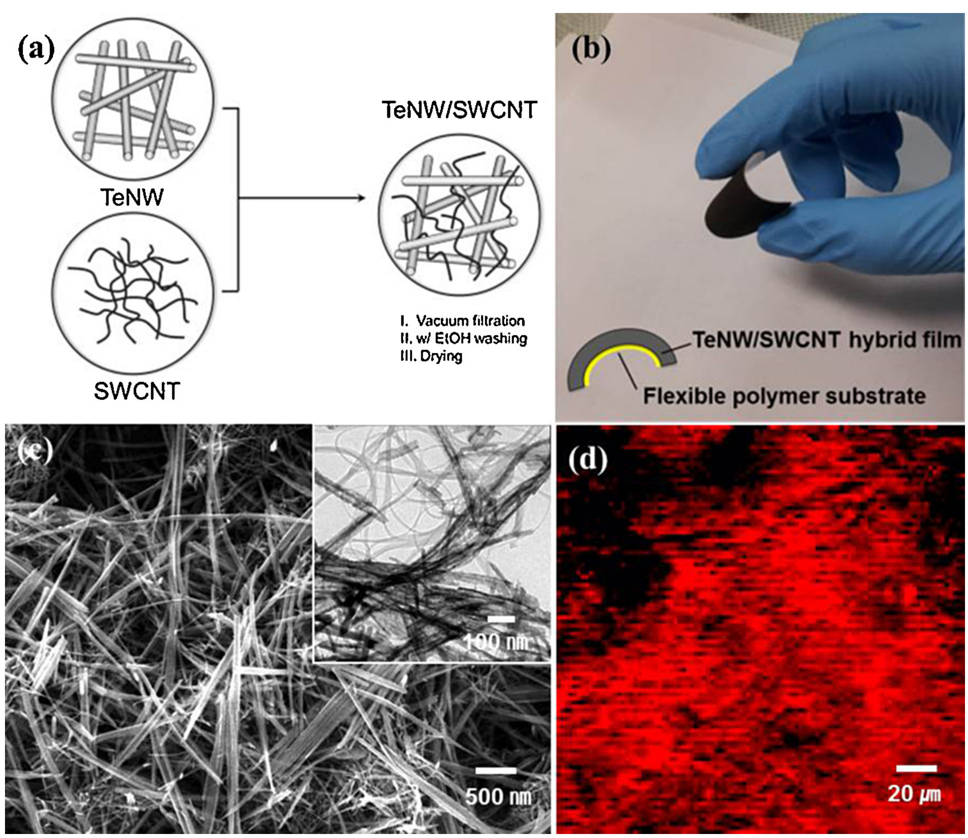


**Fig. 2.** (a) Schematic illustration for the preparation of SWCNT/TeNW hybrid film, and (b) Optical, (c) FE-SEM (Inserted image: TEM), and (d) Raman mapping images of SWCNT/TeNW film hybridized with 2 wt% of SWCNT.

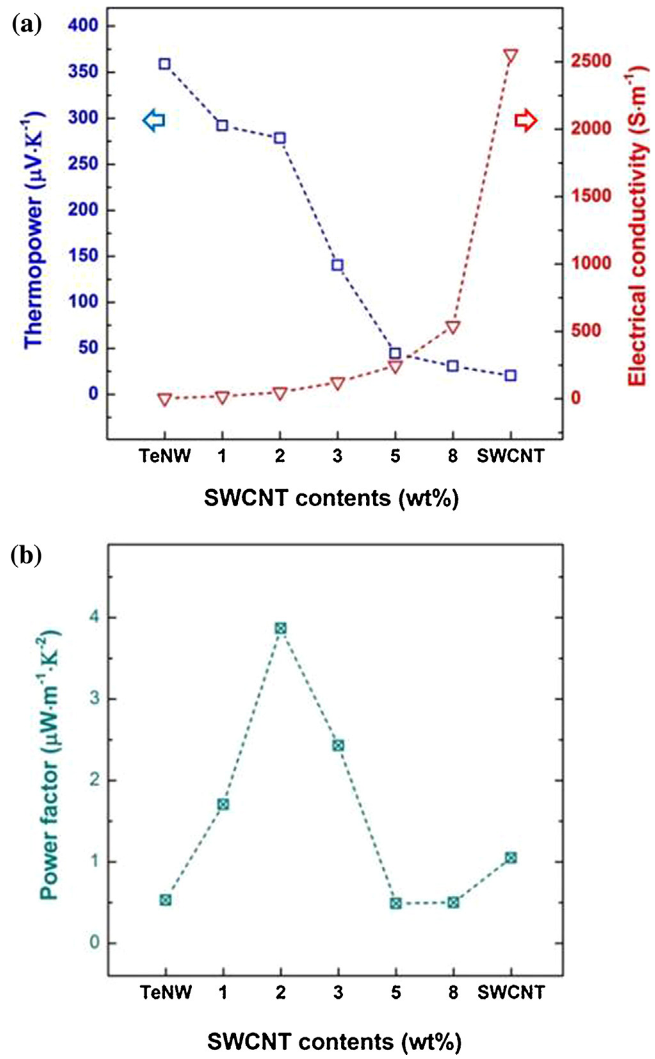


**Fig. 3.** (a) Thermopower and electrical conductivity, and (b) Power factor of SWCNT/TeNW hybrid films as a function of SWCNT contents.

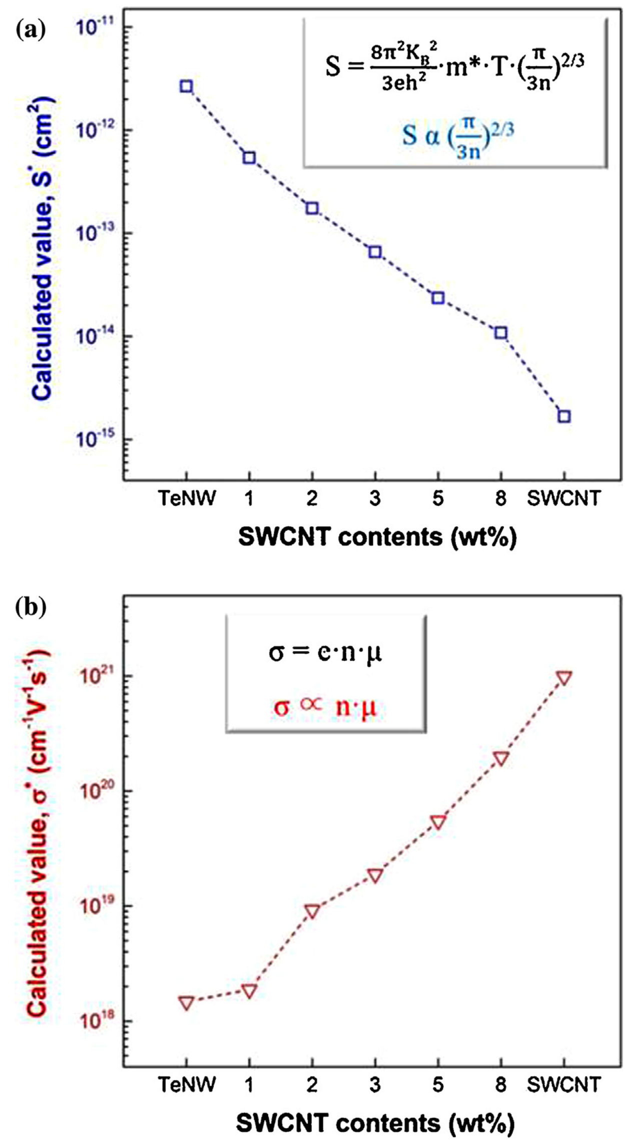


**Fig. 4.** Calculated values of the relative (a) thermopower and (b) electrical conductivity of SWCNT/TeNW hybrid films as a function of SWCNT contents.

spectrometer (invia Raman microscope, Renishaw) with 633 nm laser source of He-Ne. Electrical conductivity and thermopower of the hybrid film were measured by Seepel instrument (Model TEP 600) at 298 K. The sample size for TE measurement was 2 cm × 2 cm and sample's thickness was approximately 100 μm. When we applied the temperature differences (0.5, 1.5 and 2.5 °C in one direction, and −0.5, −1.5 and −2.5 °C in the opposite direction) to the two ends of the sample, the probes measured the potential difference and calculated the thermopowers. The in-plane thermal conductivity of the sample was obtained from the thermal diffusivity measured by laser flash system (LFA 457 NanoFlash, Netzsch), the specific heat measured by DSC (DSC7, PerkinElmer) and the density of the sample. The carrier concentration and mobility were measured by Hall measurement (HMS-3000, Ecopia).

## 3. Results and discussion

The TeNW was selected as a matrix for the hybrid film due to its high thermopower. It has been known that TeNW has relatively higher thermopower than tellurium nanoparticle because of quantum confinement effect derived from its 1-D structure [27,28]. The synthesized TeNW in SEM image of Fig. 1(a) is structurally uniform, and it has approximately 30 nm in average diameter and 3 μm in average length. The TeNW has a single-crystalline structure with the regular direction to (0 0 1) lattice plane of hexagonal Te, which is consistent with the inserted SAED (selected area electron diffraction) pattern of Fig. 1(b) [29]. Right after the synthesis, the TeNW was hybridized with SWCNT due to the high electrical conductivity and mechanical stability of SWCNT in order to improve the TE performance. The SWCNT/TeNW hybrid film was successfully prepared by a simple solution process and the schematic illustration for the preparation has been shown in Fig. 2(a). The optical image of the hybrid film in Fig. 2(b) shows that the as-prepared hybrid film is flexible and light while the TeNW film without SWCNT is very brittle. It seems that the SWCNTs with mechanical stability and high aspect ratio support the brittle structure of TeNW network, thus making the hybrid film flexible. The microstructural morphology of the hybrid film by the FE-SEM and TEM analyses shown in Fig. 2(c) indicates that the rigid TeNWs form the network to transport the carriers and the small amount of SWCNTs are doped into the TeNW matrix. The distribution of SWCNTs in the TeNW matrix was additionally characterized using Raman mapping at the characteristic G band (1578 $cm^{-1}$) of SWCNT (Fig. 2(d)). SWCNTs

**Table 1**
Electrical conductivity, thermopower, carrier concentration and carrier mobility of TeNW, SWCNT and SWCNT/TeNW hybrid films.

| Sample (SWCNT contents) | Electrical conductivity ($S\,m^{-1}$) | Thermopower ($\mu V\,K^{-1}$) | Carrier concentration ($cm^{-3}$) | Mobility ($cm^2\,v^{-1}\,S^{-1}$) |
|---|---|---|---|---|
| TeNW | 4 | 359 | $2.41 \times 10^{17}$ | $6.12 \times 10^{0}$ |
| Hybrid (1 wt%) | 20 | 292 | $2.64 \times 10^{18}$ | $7.13 \times 10^{-1}$ |
| Hybrid (2 wt%) | 50 | 279 | $1.44 \times 10^{19}$ | $6.43 \times 10^{-1}$ |
| Hybrid (3 wt%) | 123 | 140 | $6.21 \times 10^{19}$ | $3.04 \times 10^{-1}$ |
| Hybrid (5 wt%) | 247 | 45 | $2.89 \times 10^{20}$ | $1.89 \times 10^{-1}$ |
| Hybrid (8 wt%) | 541 | 31 | $9.33 \times 10^{20}$ | $2.11 \times 10^{-1}$ |
| SWCNT | 2558 | 20 | $1.54 \times 10^{22}$ | $6.38 \times 10^{-2}$ |

seem to be well-distributed in the TeNW matrix in order to uniformly add the charge carriers into the matrix.

Fig. 3(a) shows the thermopower and electrical conductivity of hybrid films as a function of SWCNT content. The thermopower and electrical conductivity of TeNW film without SWCNT are $359\,\mu V\,K^{-1}$ and $4\,S\,m^{-1}$, respectively, which are similar to the previous reports [23]. As the SWCNTs add to the TeNW matrix, the thermopower decreases and the electrical conductivity increases. The thermopower is very sensitive to the amount of SWCNT. When we add more than 5 wt% of SWCNT into the TeNW matrix, the thermopower rapidly decreases, which is close to that ($20\,\mu V\,K^{-1}$) of the pure SWCNT film. On the other hand, the electrical conductivity of the hybrid film increases from 4 to $541\,S\,m^{-1}$ with an increase of the amount of SWCNT up to 8 wt%, which is contrary to the thermopower. This trend is general in typical bulk inorganic semiconductors. Insulators and semiconductors have large thermopower due to their low carrier concentration [5]. However, low carrier concentration results in low electrical conductivity. Therefore, the increasing the electrical conductivity leads to a decrease in the thermopower. Fig. 3(b) shows the power factor calculated by $S^2\sigma$ as a function of SWCNT content in hybrid film. Power factor is a powerful parameter to find the optimum content of SWCNT in the hybrid. The hybrid film with 2 wt% SWCNT shows the maximum power factor of $3.87\,\mu W\,m^{-1}\,K^{-2}$, which is seven times and four times higher than those of pure TeNW and SWCNT film, respectively.

To deeply understand the correlation between the amount of SWCNT and TE properties of the hybrid film, we measured the carrier concentration and mobility of all samples by Hall measurement. Table 1 shows the electrical conductivity, thermopower, carrier concentration and carrier mobility of TeNW, hybrid films and pure SWCNT. The as-prepared TeNW film has relatively low carrier concentration of $2.41 \times 10^{17}\,cm^{-3}$ with high thermopower because the thermopower is in inverse proportional to the carrier concentration [5]. On the other hand, the SWCNT film has 5 orders of magnitude higher carrier concentration of $1.54 \times 10^{22}\,cm^{-3}$ compared to the as-prepared TeNW film, thus resulting in lower thermopower. As the amount of SWCNT in hybrid increases, the carrier concentration of the hybrid film increases due to SWCNT as a carrier donor, thereby leading to an increase of the electrical conductivity and decrease of thermopower. In addition, the carrier mobility slightly decreases with an increase of the amount of SWCNT in hybrid, which is consistent with the previous reports [30]. The carrier mobility of doped-semiconductor generally decreases due to an increase of the carrier density as the doping level increases [31]. For more systematic analysis of our TE data, we used the simplified forms of thermopower and electrical conductivity based on the model suggested by Snyder and Toberer [5]. According to this model, the thermopower and electrical conductivity can be presented by Eqs. (2) and (3), respectively

$$S = \frac{8\pi^2 K_B^2}{3eh^2} \times m^* \times T \times \left(\frac{\pi}{3n}\right)^{2/3} \quad (2)$$

$$\sigma = e \cdot n \cdot \mu \quad (3)$$

$K_B$, h, n, m*, $T$ and $\mu$ are the Boltzmann constant, Plank constant, carrier concentration, effective mass of the carrier, absolute temperature and carrier mobility, respectively. In order to understand the effect of carrier concentration and mobility on the thermopower and electrical conductivity, we simplify these equations without common constants and define the relative thermopower and electrical conductivity as and from Eqs. (2) and (3), respectively. As shown in Fig. 4(a) and (b), the relative thermopower and electrical conductivity are inversely and directly proportional to the content of SWCNT in hybrid, respectively, which is well matched with the experimental trends of thermopower and electrical conductivity in Fig. 3(a). It indicates that the content of SWCNT linearly increases the carrier concentration of the hybrid film, thus decreasing the thermopower without additional effects such as an energy filtering effect and increasing the electrical conductivity.

Therefore, it is important to find the optimum content of SWCNT in the hybrid with consideration for the carrier concentration, carrier mobility and thermopower, i.e. power factor, for the enhanced TE performance. In this study, the optimum content of SWCNT in the hybrid is determined to be 2 wt% (Fig. 3(b)). At this content of SWCNT, the hybrid film has the enhanced electrical conductivity with maintaining the relatively high thermopower, leading to the maximum power factor of $3.87\,\mu W\,m^{-1}\,K^{-2}$. The thermal conductivity of the hybrid film with 2 wt% SWCNT was measured to 0.26 W/mK due to the phonon scattering at the junctions of the hybrid materials [32]. As a result, the maximum ZT of the hybrid film was calculated to be $4.5 \times 10^{-3}$, which is one order of magnitude higher than that of the pure TeNW film shown in Table 2. Although the TE performance of the hybrid film is enhanced compared to the pure TeNW or SWCNT film, the absolute ZT is low due to low electrical conductivity of commercial SWCNT (mixture of metallic and semiconducting SWCNTs) used in this work. This can be further improved if pure metallic SWCNT can be applied and then the electrical

**Table 2**
Thermoelectric performance of TeNW, SWCNT and SWCNT/TeNW film hybridized with 2 wt% SWCNT.

| Sample (SWCNT contents | Electrical conductivity ($S\,m^{-1}$) | Thermopower ($\mu V\,K^{-1}$) | Power factor ($\mu W\,m^{-1}\,K^{-2}$) | Thermal conductivity ($W\,m^{-1}\,K^{-1}$) | Figure of merit ($10^{-2}$ ZT) |
|---|---|---|---|---|---|
| TeNW | 4 | 359 | 0.53 | 0.28 | 0.05 |
| SWCNT | 2558 | 20 | 1.05 | 0.42 | 0.08 |
| Hybrid (2 wt%) | 50 | 279 | 3.87 | 0.26 | 0.45 |

conductivity of the hybrid film can be increased by much higher electrical conductivity of metallic SWCNT.

## 4. Conclusion

In summary, we have demonstrated that the mechanical flexibility and TE performance of TeNW film can be improved by the hybridization with SWCNT, suggesting a potential for use as a promising thermoelectric material. The effects of the amount of SWCNT in hybrid on TE performance have been systematically studied. The addition of 2 wt% SWCNT into TeNW matrix significantly increases the electrical conductivity while maintaining the high thermopower, thereby leading to one order of magnitude higher ZT compared to the pure TeNW film. Compared to other thermoelectric materials, however, the TE property of the SWCNT/TeNW hybrid films is limited by their still low electrical conductivity. If the electrical conductivity of the hybrid film can be further improved to the level of the pure metallic SWCNT while maintaining the high thermopower, the ZT of the hybrid film would be significantly increased. Furthermore, if the thermopower can also be increased with maintaining the high electrical conductivity using an energy filtering effect at the interfaces between SWCNT and TeNW, the TE performance of the hybrid film could be more increased. Further investigation into TE properties of SWCNT/TeNW film with the energy filtering effect has been in progress.

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